Title of the Invention

HIGH-CHROMIUM NITROGEN CONTAINING CASTABLE ALLOY

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HIGH-CHROMIUM NITROGEN CONTAINING CASTABLE ALLOY

CROSS-REFERENCE TO RELATED APPLICATION

[0001] This application is a continuation-in-part of U.S. application Serial No. 10/040,357 filed January 9, 2002, the entire disclosure whereof is expressly incorporated by reference herein.

BACKGROUND OF THE INVENTION

1. Field of the Invention

[0002] This invention relates generally to the art of alloys and more particularly to a high-chromium, nitrogen containing alloy having high corrosion resistance. The instant invention also relates to a high-chromium, nitrogen containing castable alloy, a high-chromium nitrogen content alloy, and a process for producing the high-chromium, nitrogen containing alloy, and articles prepared from the same.

2. Discussion of Background Information

[0003] Equipment used in highly corrosive environments typically is made of alloys such as stainless steel and other highly alloyed materials. These alloys must be able to withstand the extremely corrosive environments created by chemicals such as concentrated sulfuric acid or concentrated phosphoric acid. A particularly difficult environment is encountered in the production of phosphate fertilizer. In the digestion of phosphate rock with hot, concentrated sulfuric acid, the equipment is required to be resistant to the environment at temperatures up to about 100° C. The crude phosphoric acid produced can be extremely corrosive and contains some residual sulfuric acid. The corrosive effect is often increased by other impurities in the phosphoric acid, particularly by halogen ions such as chloride and fluoride, which are normally present in the phosphate rock feedstock that is used in the process. A particularly corrosive environment is encountered during the concentration of the crude phosphoric acid.

[0004] Phosphate rock deposits at various locations in the world vary greatly in chemical composition. The most severe corrosive environments are typically encountered in the processing of deposits of phosphate rock which contains a high content of halides, such as chloride or fluoride.

[0005] It is known that increasing the Cr content improves the corrosion resistance of steel. Hi-chromium alloys containing 23-40 % Cr, 0.8-2 % C, 2.5 % Si, and up to 5 % Mo, have been known since the 1930's. See, for example, German Patent No. 701,807. U.S. Patent No. 5,252,149 represents an improvement of this alloy, followed by German Patent Application Nos. 195 12 044 and 44 17 261. According to both patents the alloys exhibit a high resistance to abrasion and good resistance to corrosion. However, both alloys exhibit poor mechanical properties, especially low toughness, brittleness, sensitivity to heat, and low notched impact resistance, thereby limiting their usefulness. It is evident that their structures comprise ferrite (Fe-α).

[0006] The ferritic structure comprised in these alloys is inherently very brittle, and the carbide phase embedded in such a brittle phase results in a very low toughness, high notch sensitivity, as well as sensitivity to heat. Additionally, the ferritic structure is supersaturated with chromium, resulting in a formation of the sigma phase, which drastically lowers toughness and corrosion resistance.

[0007] U.S. Patent No. 5,320,801 is directed to alloys having the following composition in % by weight : Cr – 27 to 34, Ni + Co – 13 to 31, Si – 3.2 to 4.5, Cu – 2.5 to 4, C – 0.7 to 1.6, Mn – 0.5 to 1.5, Mo – 1 to 4, and Fe – essentially the balance. The alloy of the '801 patent possesses good toughness, but exhibits very poor hardness and very poor wear resistance and low tensile strength. Its hardness of 208 to 354 HB is similar to that of CD4MCU stainless steel (260-350 HB), which has excellent corrosion resistance, but poor wear resistance. The alloy disclosed in U.S. Patent No. 5,320,801 is similar to austenitic, high-nickel stainless steels in that it has good toughness, but very low tensile strength and hardness, as well as poor wear resistance. The nickel present in corrosion resistant alloys mainly assists in structural stabilization but contributes very little to an improvement in corrosion resistance. Representative examples thereof are the stainless austenitic steels which contain 12 – 35 % Ni and have a corrosion resistance which approaches that of duplex stainless steels which contain a low percentage of nickel (4-8 %), or that of high-chromium stainless steels with a Ni content of not more than 4 %. The primary elements of stainless alloys are Cr, Mo and nitrogen, as shown in the Examples below which illustrate how various alloying elements influence the corrosion resistance of stainless steel. For example, the Pitting Resistance Equivalent Number (PREN) = % Cr

+ 3.3 x % Mo + 16 x % N illustrates that nitrogen is an important, very powerful alloying element of corrosion resistant alloys.

[0008] One of the main shortcomings of the high-chromium alloys of the prior art is the difficulty in dissolving Cr, Mo and N in the matrix without adversely affecting the mechanical properties of the alloy, such as toughness, tensile strength, brittleness, heat sensitivity and weldability. This difficulty is due to the precipitation of the sigma phase from alloys which are saturated with chromium and molybdenum. Premature wearing out of pump parts made from the above-mentioned high-chromium alloys is a common occurrence. The main contributing factors in this respect are very low toughness, brittleness and low endurance. Very often a failure occurs due to a casting which is worn thin in an isolated area where, due to the poor mechanical properties of the alloy, a crack developed. Eventually, this leads to the destruction of an otherwise still viable component.

[0009] The mechanisms of corrosion and erosion in acidic environments of the alloys of the prior art involve accelerated corrosion due to the continuous removal of the passive corrosion resistant layer by particles contained in corrosive fluids. This is most evident in alloys which contain a higher content of Cr and Mo, where a significant amount of sigma phase is unavoidable and the metal matrix possesses very poor toughness properties. In order to restore the passive layer, it is necessary to use as high as possible concentrations of Cr and Mo.

[0010] An increase in the Cr/C, or (Cr + Mo)/C ratio increases the corrosion resistance up to the critical point, after which the formation of the sigma phase begins, which drastically reduces the toughness and lowers the corrosion resistance of the alloy by depleting the Cr in the vicinity of the sigma phase precipitates.

[0011] The present invention provides an increase in the ratio (Cr + N)/(C - N), or (Cr + Mo + N)/C and (Cr + Mo + N + B)/(C - N) by reducing the carbon content in the matrix and introducing nitrogen as a powerful additional alloying element to the high-chromium alloys, where it is present in a high concentration in solid solution.

[0012] Nitrogen, like carbon, forms interstitial solids with body-centered-cubic (bcc) α-iron, and face - centered - cubic (fcc) γ- iron. The size of the nitrogen atom is smaller

than that of the carbon atom, wherefor the nitrogen atom can occupy the interstitial sites in the α- as well as in the γ- phases more easily than the carbon atom.

[0013] The maximum solubility of nitrogen in Fe-α and Fe-γ is several times higher than that of carbon at the same temperature, which leads to a substantial expansion and distortion of elementary lattices. Nitrogen has a solid solution hardening and strengthening effect that is much greater than that of carbon, while at the same time maintaining a higher level of toughness.

[0014] The solubility limits of nitrogen in the prior art high-chromium alloys are a very low, 0.15 % of N at the most. This limit is dictated by the inherently low physico-chemical solubility of nitrogen and carbon (0.02 to 0.08 % max. for C + N) in the Fe-α structure, which constitutes up to a maximum of 40 % of the alloys of German Patent Application Nos. 44 17 261 or 195 12 044 as well as by a low Mn content of ≤ 1.5 %.

[0015] The addition of nitrogen is the most effective means for improving the mechanical properties of austenitic high-chromium alloys without deleteriously affecting the ductility and corrosion resistance thereof. It has now been found that if Mn and/or Mo are present in considerable amounts in high-chromium alloys, nitrogen can be fully effective as an anti-corrosive agent, and may have a wide range of positive effects on the mechanical properties of a casting such as, e.g., increased tensile strength, hardness and toughness, without giving rise to a loss in ductility. In particular, under these conditions nitrogen dissolves in the solid state two to four times better than in any other high-chromium alloy of in the prior art. Similarly, in high- manganese stainless steels, which dissolve up to 0.8 % nitrogen, and even up to 1 % under high nitrogen partial pressure, the tensile strength and the hardness may be increased by a factor of two to four, with as good a ductility as for the same steel without nitrogen.

SUMMARY OF THE INVENTION

[0016] The present invention provides a corrosion and erosion resistant alloy which comprises, in % by weight, about 31 to about 48 chromium, about 0.01 to about 0.7 nitrogen, about 0.5 to about 30 manganese, about 0.3 to about 2.5 carbon, 0 to about 5 boron, 0 to about 6 molybdenum, 0 to about 5 silicon, 0 to about 8 copper, 0 to about 4

cobalt and 0 to about 25 nickel plus cobalt. This alloy further comprises 0 to about 2 % of each of zirconium, vanadium, cerium, titanium, tantalum, tungsten, niobium, aluminum, calcium and rare earth elements, the balance comprising iron and inevitable impurities. It has a microstructure which comprises chromium carbides, nitrides and optionally borides in an austenitic matrix, which matrix has a face centered cubic structure and is supersaturated with nitrogen in solid solution form. The composition of the alloy satisfies the relationship:

$$\frac{\% Ni + \% Co + 0.5(\% Mn + \% Cu) + 30(\% N + \% C) + 5x\% B}{\% Cr + \% Mo + \% Si + 1.5(\% Ti + \% Ta + \% V + \% Nb + \% Ce + \% Al)} \geq 1.5 .$$

[0017] In one aspect, the alloy may comprise molybdenum, silicon, boron, copper and/or (nickel plus cobalt), each in an amount of at least about 0.01 % by weight.

[0018] In another aspect, the alloy may have a PREN of from 58 to 66 and/or the matrix may comprise from about 0.25 % to about 0.45 % of nitrogen in solid solution form.

[0019] In yet another aspect, the alloy may comprise at least about 32 % by weight of chromium.

[0020] In a still further aspect, the alloy may comprise about 32 to about 34 chromium, about 0.35 to about 0.45 nitrogen, about 6 to about 9 manganese, about 0.5 to about 2.5 carbon, 0 to about 4.5 boron, 0 to about 5 molybdenum, 0 to about 3 silicon, 0 to about 4 copper, 0 to about 4 cobalt and 0 to about 4 nickel plus cobalt. This alloy may comprise about 2 to about 5 molybdenum, about 0.5 to about 3 silicon, about 0.7 to about 4 copper and/or about 1.5 to about 4 nickel plus cobalt. For example, about 2 to about 4 molybdenum, about 0.5 to about 2 silicon, about 0.7 to about 3 copper and about 1.5 to about 3 nickel plus cobalt may be present in this alloy. Moreover, the alloy may comprise at least about 0.01 % by weight of boron.

[0021] In a still further aspect, the alloy of the present invention may comprise, in % by weight, about 35 to about 40 chromium, about 0.4 to about 0.6 nitrogen, about 4.5 to about 15 manganese, about 0.8 to about 1.6 carbon, 0 to about 5 boron, 0 to about 5 molybdenum, 0 to about 3 silicon, 0 to about 6 copper, 0 to about 4 cobalt and 0 to about 13 nickel plus cobalt. This alloy may comprise, for example, about 2 to about 4

molybdenum, about 0.5 to about 2 silicon, about 1 to about 4 copper and/or about 4 to about 13 nickel plus cobalt, e.g., it may comprise about 0.9 to about 1.6 carbon, about 5 to about 13 manganese, about 2 to about 4 molybdenum, 0 to about 4.5 boron, about 0.5 to about 1.5 silicon, about 1 to about 3 copper, about 0.01 to about 4 cobalt, and about 4 to about 12.5 nickel plus cobalt, or it may comprise about 1 to about 1.55 carbon, about 5 to about 12 manganese, about 2 to about 3.5 molybdenum, 0 to about 4 boron, about 0.6 to about 1.2 silicon, about 1 to about 2.5 copper, about 0.02 to about 4 cobalt and about 4 to about 12 nickel plus cobalt. This alloy may have a PREN is from 58 to 66 and/or the matrix thereof may comprise from about 0.25 % to about 0.45 % by weight of nitrogen in solid solution form.

[0022] In yet another aspect of the alloy of the present invention, the alloy may comprise, in % by weight, about 41 to about 48 chromium, about 0.45 to about 0.7 nitrogen, about 6 to about 30 manganese, about 0.9 to about 1.5 carbon, 0 to about 3.5 boron, 0 to about 4 molybdenum, 0 to about 3 silicon, 0 to about 8 copper and 0 to about 25 nickel plus cobalt. This alloy may comprise, for example, molybdenum, silicon, boron, copper and/or (nickel plus cobalt), each in an amount of at least about 0.01 % by weight. Particularly, this alloy may comprise about 1 to about 4 molybdenum, about 0.5 to about 3 silicon, about 1 to about 8 copper and about 10 to about 25 nickel plus cobalt. Also, it may have a PREN of from 51 to 72 and/or the matrix thereof may comprise from about 0.25 % to about 0.45 % by weight of nitrogen in solid solution form.

[0023] The present invention also provides a casting of the alloy of the present invention, including the various aspects thereof. For example, the casting may be a casing, impeller, suction liner, pipe, nozzle, agitator or a valve blade.

[0024] The present invention provides a high-chromium alloy and, more specifically, a corrosion and erosion resistant high-chromium, nitrogen containing castable alloy. The alloy of the present invention may be used, for example, for the manufacture by casting of slurry pump parts, such as casings, impellers, suction liners, pipes, nozzles, agitators, valve blades, in particular, for casting parts will be exposed to highly corrosive fluids and abrasive slurries. A typical application for such parts is in the wet processing of phosphoric acid. Industrial phosphoric acid solutions are chemically complex, containing sulfuric acid, hydrofluoric acid, hydrochloric acid, chlorides, fluorides and gypsum, all

highly depassivating species which are highly detrimental to the parts exposed thereto. Another application for such parts is in power plant scrubbers i.e., flue gas desulfurization processes where the parts are exposed to sulfuric components and gypsum.

[0025] One of the objects of the present invention is to provide a material with high resistance to chloride environments, which at the same time exhibits extraordinary properties in acidic and basic environments, combined with good mechanical properties and high structural stability. This combination can be very useful in applications in, for example, the chemical industry, where problems exist with respect to corrosion caused by acids, and a contamination of the acids with chlorides amplifies the corrosive effect. These properties of the alloy in combination with a high strength lead to advantageous design solutions from an economic point of view. Currently available materials with good properties in acidic environments include steels with high contents of Ni, which makes these materials very expensive. Another disadvantage of austenitic steels is that they usually exhibit a very low strength.

[0026] It has been found that the maximum solubility of nitrogen in a solid solution of the FeCr-Mn alloys of the present invention is about 0.013 to about 0.0155 % N with 1 % of Cr and a minimum of 6 % of Mn and a minimum of 2 % of Mo as the best enhancement.

[0027] Nitrogen has a much lower affinity toward Cr than carbon. The above-mentioned properties of nitrogen in high-chromium-manganese alloys cause the carbon in these alloys to be transformed into the carbide phase, forming hard eutectic chromium carbides, with the surplus carbon being dissolved in the matrix together with nitrogen.

[0028] Nitrogen introduced in a high concentration in solid solution has a much stronger effect than carbon on the retardation of the formation the sigma phase, thereby allowing larger quantities of Cr and Mo to be dissolved in the Fe-Cr-Mn alloys to enhance passivation.

[0029] Nitrogen generally improves corrosion resistance, particularly in chloride containing media. In stainless steels its effectiveness has been tested and expressed by the PREN value (Pitting Resistance Equivalent Number) = % Cr + 3.3 x % Mo + 16 x % N.

The higher the level of the passivating elements (Cr, Mo, N), the higher the resistance to corrosion/erosion.

[0030] Additionally, boron reacts with many elements in the Periodic Table to form a wide variety of compounds. The strong covalent bonds of most borides are responsible for their high melting points, corrosion resistance and hardness values. The chemical resistance of borides is superior to that of most of their nitride and carbide counterparts. Because of the larger atomic size of $B \approx 0.91Å$, compared to $C \approx 0.77Å$ and $N \approx 0.71Å$, interstitial substitution of boron in an undistorted octahedral site is rare, resulting primarily in boron - boron bonding, for borides M_nB_m (NiB, CoB, MnB, FeB, CrB)

[0031] In addition, nickel, manganese and iron react strongly with boron and form very hard compounds, much harder than the corresponding nitrides or carbides. For extremely abrasive and corrosive applications boron is preferably employed in concentrations of up to about 5 % B, with a carbon content of from about 0.3 % to about 1.2 % and a nitrogen content of form about 0.4 % to about 0. 6 %.

[0032] Overall superior results are realized according to the present invention by the novel microstructure, with a highly corrosion-resistant matrix, preferably austenitic, of face centered cubic crystal structure, and supersaturated by nitrogen in solid solution form. This matrix is very hard, tough, non-brittle and has carbides and nitrides (and optionally borides) embedded therein, which additionally imparts high wear resistance to the matrix.

[0033] In practicing the instant invention, it is preferred for the matrix to contain high levels of Cr, Mo and N in a solid solution, without Cr, or Mo, being trapped by sigma phase precipitates. It is desired that the constituting elements of the alloys of the present invention satisfy the following relationship, which is a measure of the austeniticity of the present alloys:

$$\frac{\%Ni + \%Co + 0.5(\%Mn + \%Cu) + 30(\%N + \%C) + 5x\ \%B)}{\%Cr + \%Mo + \%Si + 1.5\ (Ti + Ta + V + Nb + Ce + Al)} \geq 1.5$$

[0034] Due to the addition of the austenite-formers nickel and cobalt in a concentration range of about 0.01 % to about 25 wt.-%, it is possible to control the ratio of the ferrite

and austenite phases in the matrix in a defined manner. The normally extremely high brittleness of chilled casting types with high carbon contents and a carbide lattice in a ferritic matrix is avoided by the predominant deposition of the chromium carbides in the only phase present, i.e., the austenitic phase. Since the austenitic phase, unlike the ferrite phase, is not embrittled by segregation of intermetallic phases or by segregation processes, the danger of fractures due to stresses between the carbides and the matrix is not as great as it is in the case of a purely ferritic or ferritic-austenitic matrix.

[0035] A molybdenum content within the range of from about 0.01 % to about 6 weight %, preferably from about 2 % to about 4 weight %, and especially about 2 % to about 3 weight %, increases the corrosion resistance, especially in chloride-containing, acidic media.

[0036] Also, by varying the alloy components carbon and chromium within the range of from about 0.3 % to about 2.5 weight % for carbon and from about 31 % to about 48 weight % for chromium, the corrosion resistance and wear resistance of the material of the invention can be adjusted to correspond to a prescribed specification profile.

[0037] The corrosion resistant high-chromium, nitrogen containing austenitic alloy of the present invention has excellent high temperature strength and is suitable as construction material for boilers, chemical plant reactors and other equipment which is regularly exposed to high temperatures and/or corrosive environments. The present invention also provides a metal casting material the wear resistance of which corresponds approximately to that of materials of common commercial types of white iron, and which additionally exhibits high corrosion resistance in aggressive media. In addition to high corrosion and wear resistance, the alloy according to the invention has good casting characteristics. Accordingly, it can be produced in conventional high-grade steel foundries. The casting material also has good working characteristics. These advantageous characteristics of the alloy of the present invention may be attributed primarily to a chromium content of about 31 to about 48 wt. %, a carbon content of about 0.3 to about 2.5 wt. %, and a nitrogen content of about 0.01 to about 0.7 wt. %, which affords a sufficiently high volume proportion of carbides and nitrides. The high-chromium content decreases the chromium depletion of the matrix. Compared to the known types of castings previously utilized in applications involving hydroabrasive wear,

the material according to the present invention shows a much better combination of corrosion resistance and wear resistance. The present invention is also directed to an air-meltable, castable, workable alloy which exhibits resistance to the corrosive action of acids such as sulfuric acid and phosphoric acid over a wide range of acid strengths.

[0038] The high-chromium, nitrogen containing alloy composition of the present invention is also highly responsive to a cryogenic hardening process, thereby becoming super-hard. When hardened by the cryogenic treatment, the composition possesses higher abrasion resistance, greater hardness, and a durable matrix without the usual precipitation of secondary carbides.

[0039] The alloys of the invention may be prepared by conventional methods of melting, and no special conditions, such as, e.g., controlled atmosphere, special furnace linings, protective slags or special molding materials are required.

[0040] In the treatment process of the present invention, the high-chromium, nitrogen containing castable alloy has many of the alloying elements entirely distributed in the austenitic phase or its transformation products, when subjected to sub-zero treatment of at least -100° F, preferably –100° F to –300° F, attain much greater hardening than that achieved through conventional high temperature treatments.

[0041] Generally, the high-chromium, nitrogen containing alloys of this invention are made by preparing a molten metal mass of all the required elements in the presence of air or additional nitrogen, pouring castings therefrom, cooling of the castings, and subjecting the castings to a cryogenic cooling treatment to produce the desired hardness. The surface of the casting may be cleaned and finished, either before or after cryogenic cooling. In more detail, the preferred process involves the following steps:

(1) mixing the necessary components to be fed to the furnace;

(2) melting the mixture in the furnace to form a pourable molten metal;

(3) pouring the molten metal composition into an appropriate mold;

(4) allowing the mold and the casting therein to cool slowly to room temperature under ambient conditions;

(5) cleaning and finishing the surface of the casting, for example, by grinding or the like to smooth the surface; and,

(6) immersing the finished casting in a cryogenic cooling medium at a temperature of -100° F to -300° F for a time sufficient to reach the desired hardness.

DETAILED DESCRIPTION OF THE PRESENT INVENTION

[0042] The particulars shown herein are by way of example and for purposes of illustrative discussion of the embodiments of the present invention only and are presented in the cause of providing what is believed to be the most useful and readily understood description of the principles and conceptual aspects of the present invention. In this regard, no attempt is made to show structural details of the present invention in more detail than is necessary for the fundamental understanding of the present invention, the description making apparent to those skilled in the art how the several forms of the present invention may be embodied in practice.

[0043] Several mechanical tests as described below were conducted which included the following measurements:

Tensile Strength - (Ksi)

Deflection - (mm), 30.5 mm diameter cast bar, 300 mm span.

Impact Resistance - (J), IZOD test, unnotched 30.5 mm diameter bar, struck 76 mm above support.

Hardness - (BHN): Brinell test, 3000 kg load on 10 mm tungsten carbide ball.

For the testing, alloys according to the present invention were compared to alloys of the prior art alloys, and stainless steel as a reference.

[0044] The specific alloys tested were as follows:

[0045] Preferred alloys (composition in wt. %) of U.S. Patent No. 5,252,149:

1	2	3
Cr 36.6	Cr 38.2	Cr 39.3
C 1.9	C 2.06	C 2.02
Mn 1.2	Mn 1.5	Mn 1.1
Si 1.5	Si 1.4	Si 1.5
Ni 2	Mo 1.2	Mo 1.8
Cu 1	Ni 1.2	Ni 1.6
Balance - Fe plus	Cu 1.2	Cu 1.6

inevitable impurities		
	Balance - Fe plus inevitable impurities	Balance - Fe plus inevitable impurities

[0046] Preferred alloys (composition in wt. %) of U.S. Patent No. 5,320,801:

4	5	6
Cr 29.8	Cr 32.7	Cr 34.8
Ni+Co 17.2	Ni+Co 26.5	Ni+Co 34.5
Si 3.4	Si 3.2	Si 3.5
Cu 1.9	Cu 3.1	Cu 3.8
C 1.65	C 1.28	C 1.26
Mn 1.1	Mn 1.5	Mn 1.6
Mo 0.9	Mo 1.8	Mo 2.2
Balance - Fe plus inevitable impurities	Balance - Fe plus inevitable impurities	Balance - Fe plus inevitable impurities

[0047] Alloys according to the present invention (composition in wt. %):

7	8	8B	9	9a*	9b*
Cr 35.8	Cr 37.3	Cr 37.9	Cr 38.3	Cr 39.1	Cr 33.4
N 0.42	N 0.48	N 0.4	N 0.52	N 0.56	N 0.41
Mn 6.1	Mn 9.8	Mn 5.2	Mn 11.1	Mn 8.2	Mn 5.1
C 1.26	C 1.33	C 1.33	C 1.41	C 1.55	C 2.2
B 0.2	B 0.15	B 3.8	B 0.1	B 0	B 0
Mo 3	Mo 2.6	Mo 2.6	Mo 2.2	Mo 2.1	Mo 2.7
Si 0.9	Si 0.8	Si 1	Si 0.7	Si 0.7	Si 0.94
Cu 1.5	Cu 1.7	Cu 1	Cu 1.9	Cu 1.5	Cu 0.8
Co 2.1	Co 0.6	Co 0.5	Co 4	Co 0.02	Co 0.004
Ni 3.25	Ni 3.6	Ni 8.2	Ni 0.2	Ni 11.0	Ni 1.8
Balance - Fe plus inevitable impurities	Balance - Fe plus inevitable impurities	Balance - Fe plus inevitable impurities	Balance - Fe plus inevitable impurities	Balance - Fe plus inevitable impurities	Balance - Fe plus inevitable impurities

* = not tested

[0048] Alloys of German Patent Application Nos. 19512044 and 4417261 (composition in wt. %):

10	11	12
Cr 38.8	Cr 43	Cr 44
Ni 5	Ni 8	Ni 10
Mo 2	Mo 3	Mo 3.5
Cu 2	Cu 2.5	Cu 2.1
N 0.19	N 0.09	N 0.15
Si 1	Si 1.5	Si 1.5
Mn 1	Mn 1.2	Mn 1.1
C 1.6	C 1.7	C 1.6
V 1.2		
Balance - Fe plus inevitable impurities	Balance - Fe plus inevitable impurities	Balance - Fe plus inevitable impurities

[0049] Stainless Steel Alloy (composition in wt. %):

20Cb3	Cd-4MCu+N	317L
Cr 20	Cr 26.5	Cr 18
Ni 37.5	Ni 5.5	Ni 11
Mo 3	Mo 2.5	Mo 3.1
Cu 3	Cu 2.9	C Min.
Nb 0.4	N 0.23	
C Min	C Min	
Balance - Fe plus inevitable impurities	Balance - Fe plus inevitable impurities	Balance - Fe plus inevitable impurities

Table 1

Sample No. U.S. Pat No.	Tensile Strengt h (Ksi)	Elongation %	Deflection (mm)	Impact (J)	Hardness (BHN)	Comments
5,252,149						
1	61	0	2 / 3	12 19	450	as cast
2	64	0	1.3 / 1.9	11 18	460	
3	58	0	0.9 -1.9	10 16	490	Heat treatment at 1450 °F for 3 hrs

5,320,801						
4	53	0	8-11	22-26	360	Sample:
5	54	0.3 -- 0.6	9-13	26 - 34	330	Hardened at 1400 °F for 4 hrs
6	48	0.3 0.5	8-13	22 31	320	Hardened at 1400 °F for 4 hrs
Present invention						
7	95	0.5 – 1.1	14 - 18	48 - 59	512	Cryogenic C hardened at -300°F
8	111	0.4 – 1.0	10 - 16	41 - 49	450	Heat Treated
8B	109	0	8-12	30-36	530	as cast
9	95	0.3 – 0.6	9 – 12	36 - 47	490	as cast
German Patent Appls. 4417261, 19512044						
10	68	0	1.5 – 2.2	11 - 16	500	Heat treatment at 1800 °F for 2 hrs
11	65	0	1 2.0	10 - 15	450	
12	64	0	0.6 1.6	8 - 14	490	
Sample No. U.S. Pat No.	Tensile Strength (Ksi)	Elongation %	Deflection (mm)	Impact (J)	Hardness (BHN)	Comments

[0050] The alloys 1, 2, 3, 10, 11 and 12 of the prior art have an eutectic microstructure where the matrices are essentially ferritic (Fe-α).

[0051] The alloys according to German Patent Application Nos. 4417261 or 19512044, identified as 10, 11 and 12, can have up to 40 % or Fe-α phase in the matrix. The Fe-α phase in the high-chromium alloys inherently posses very low toughness because of the very low solubility of carbon and nitrogen in the Fe-α. Even a small, limited addition of

nitrogen has a detrimental effect on the toughness, deflection and heat sensitivity, making the alloy more brittle.

[0052] Alloys 4, 5 and 6 of U.S. Patent No.5,320,801 are chromium high-nickel alloys with an austenitic microstructure. These high-nickel alloys inherently possess a very low tensile strength, a very low hardness, as cast above 200 HB, and after hardening from the range of 300 HB, they lose their toughness and corrosion resistance.

[0053] As can be appreciated from Table 1 above, alloys 7, 8 and 9 of the present invention possess the following properties in comparison to prior art alloys:

- 2 to 3 times greater toughness
- 1.6 to 2.3 times higher tensile strength
- Very high as cast hardness after cryogenic hardening
- Measurable elongation or malleability
- Excellent deflection
- 1.5 to 2.5 higher max. hydraulic pressure vessel test.
- Low heat sensitivity
- Good machinability, especially threadability, which is very poor in prior art alloys
- Best castability with melting and pouring temp. - 150° F lower

[0054] The alloys of the prior art as well as the alloys of the present invention were subjected to corrosion test to show the superiority of the alloys of the instant invention:

[0055] The corrosion tests were conducted in synthetic P_2O_5 acid at 80° C, with a chloride content of from 1000 to 3000 ppm. Agitated, 96 hr test. (mmy). The results of the corrosion tests are summarized in Table 2.

Table 2

Sample No. Patent No.	Hardness (BHN)	Chloride Content (PPM)	Corrosion Rate (mmy)	PREN = %Cr + 3.3 x %Mo + 16x%N
US 5,320,801 5 As cast	260	1000 2000 3000	17 28 56	$PREN_5$ = 38
5 Hardened At 1400° F/4 hr	330	1000 2000 3000	23 36 65	

US 5,252,149 2 as cast	460	1000 2000 3000	15 23 49	$PREN_2 = 42$
Present Invention 8 As Cast	450	1000 2000 3000	8 11 16	$PREN_8 = 53$
Stainless Steel 20Cb-3	180	1000 2000 3000	13 14 32	PREN = 30 (20Cb-3)
Stainless Steel CD-4MCuN	280	1000 2000 3000	11 15 19	PREN = 38
CD-4MCuN Hardened	330	1000 2000 3000	17 28 45	
Stainless Steel 317L	185	1000 2000 3000	0.68 1.1	PREN = 38 (317L)

[0056] The following conclusions can be drawn from Table 2:

[0057] The high-chromium alloy No. 5 of U.S. Patent No. 5,320,801 containing 26 % Nickel has a lower corrosion resistance than alloy No. 2 of U.S. Patent No. 5,252,149, which has a nickel content of only 1 %.

[0058] The same conclusion applies to the stainless steel alloy 20Cb3, in which the Ni content is 37 %. The alloy CD4MCuN contains only 5 % Ni. The main function of Ni in corrosion resistant alloys is as a structural component.

[0059] The high-chromium, nitrogen containing alloy No. 8 of the present invention contains only 3.6 % Ni, but 0.48 % nitrogen, which is a very powerful corrosion inhibitor. Nitrogen interacts with the chlorides and somehow buffers their detrimental effect on the alloy. Alloy No. 8 according to the present invention with the higher PREN = 53, has a 2 to 3 times better corrosion resistance than the prior art alloys No. 5 and No. 2. Alloy No. 8 of the present invention which contains high levels of Cr, Mo and a high concentration of nitrogen, possesses the best corrosion resistance in acidic environments which contain high levels of chlorides.

[0060] Prior art alloys and the alloys of the present invention were also subjected to corrosion/ erosion tests as described below.

Corrosion/Erosion Test

[0061] The corrosion erosion tests were done using 30 % by weight of alumina (80 microns) suspended in 28 % P_2O_5 synthetic acid, 1.5 % H_2SO_4, 0.05 % hydrofluoric acid plus 1000 ppm Cl, temperature 800°C, rotation 650 RPM, duration 12 hr. Mass loss (mg). The results of the erosion/ corrosion testing are shown in Table 3 below.

Table 3

Sample No.	Hardness BMN	Weight Loss (mg)	PREN = CR% + 3.3 x Mo% + 16xN
U.S. Pat. 5,320,801 5 as cast	260	306.6	
5 age hardened at 1400°F/4 hr.	330	282.6	PREN (5) = 38
Present invention 8 - B 8 as cast	530 450	96.3 123.3	PREN (8B) = 53
8 anneal/S solution at 2000° F/4 hr.	450	125.1	PREN (8) = 53
Stainless Steel CD4McuN solution annealed	280	426	PREN = 38 (CD-4mcUn)
CD-4MCuN age hardened	330	328.2	
20cb – 3 solution annealed	180	660.3	PREN = 30 (20Cb-3)

[0062] The slurry corrosion/erosion tests indicate that alloy 20Cb-3 which has the lowest hardness shows the highest mass loss. Prior art alloy No. 5 has a low hardness, comparable to the hardness of the reference stainless steel CD-4MCuN.

[0063] The loss of mass of alloy No. 5 of U.S. Patent No. 5,320,801 is 50 % less than that of the stainless steel alloy Cd4MCuN. With alloy sample No. 8 according to the present invention the loss of mass is 245 % less than that of the reference alloy Cd4MCuN. Alloy No.8 with the highest PREN factor = 53, possesses the highest corrosion/erosion resistance, i.e., about 3.5 times better than that of the reference alloy CD4MCuN and 2.3 times better than that of alloy No. 5 according to U. S. Patent No. 5,320,801.

[0064] Alloy No. 8B with boron according to the present invention with the highest hardness and PREN=53 possesses the highest corrosion/erosion resistance, i.e., about 4.4 times better than that of the reference alloy CD-4MCuN and 2.9 times better than that of alloy No. 5 according to U.S. Patent No. 5,320,801.

[0065] Any conventional or under nitrogen partial pressure casting technology may be used to produce the alloys of the present invention.

[0066] It is preferred that the alloys are formed by a conventional casting technology and then are heat-treated at a temperature in the range of 1800° to 2000° F, followed by air cooling.

[0067] The most preferred hardening method for the alloy of the present invention is by cryogenic treatment: cooling to at least from -100° F to -300° F, and maintaining at these temperatures for a time of one hour per one inch of casting wall thickness.

[0068] The cryogenic tempering process may be performed with equipment and machinery which is conventional in the thermal cycling treatment field. First, the articles-under-treatment are placed in a treatment chamber which is connected to a supply of cryogenic fluid, such as liquid nitrogen or a similar low temperature fluid. Exposure of the chamber to the influence of the cryogenic fluid lowers the temperature until the desired level is reached. In the case of liquid nitrogen, this is about -300° F (i.e., 300° F below zero).

[0069] It is noted that the foregoing examples have been provided merely for the purpose of explanation and are in no way to be construed as limiting of the present invention. While the present invention has been described with reference to exemplary embodiments, it is understood that the words which have been used herein are words of

description and illustration, rather than words of limitation. Changes may be made, within the purview of the appended claims, as presently stated and as amended, without departing from the scope and spirit of the present invention in its aspects. Although the present invention has been described herein with reference to particular means, materials and embodiments, the present invention is not intended to be limited to the particulars disclosed herein; rather, the present invention extends to all functionally equivalent structures, methods and uses, such as are within the scope of the appended claims.